Electronic Supplementary Information

Investigation of the electrophilic reactivity of the cytotoxic marine alkaloid discorhabdin B

Cary Lam, Tanja Grkovic, A. Norrie Pearce, and Brent R. Copp*

School of Chemical Sciences, The University of Auckland, 23 Symonds Street, Auckland 1142, New Zealand.

b.copp@auckland.ac.nz

Contents:

S21 **Fig. S19.** HMBC NMR spectrum (CD_3OD) of **13**.
S22 **Fig. S20.** ^{1}H NMR spectrum (CD_3OD, 600 MHz) of **17**.
S23 **Fig. S21.** ^{13}C NMR spectrum (CD_3OD, 150 MHz) of **17**.
S24 **Fig. S22.** LR-COSY NMR spectrum (opt for 2 Hz, CD_3OD) of **17**.
S25 **Fig. S23.** Edited HSQC NMR spectrum (CD_3OD) of **17**.
S26 **Fig. S24.** HMBC NMR spectrum (CD_3OD) of **17**.

Fig. S1. ^{1}H NMR spectrum of **17** TFA salt in CD_3OD (600 MHz) showing 1-substituted-discorhabdin D- (blue) and discorhabdin W-type (red) resonances.

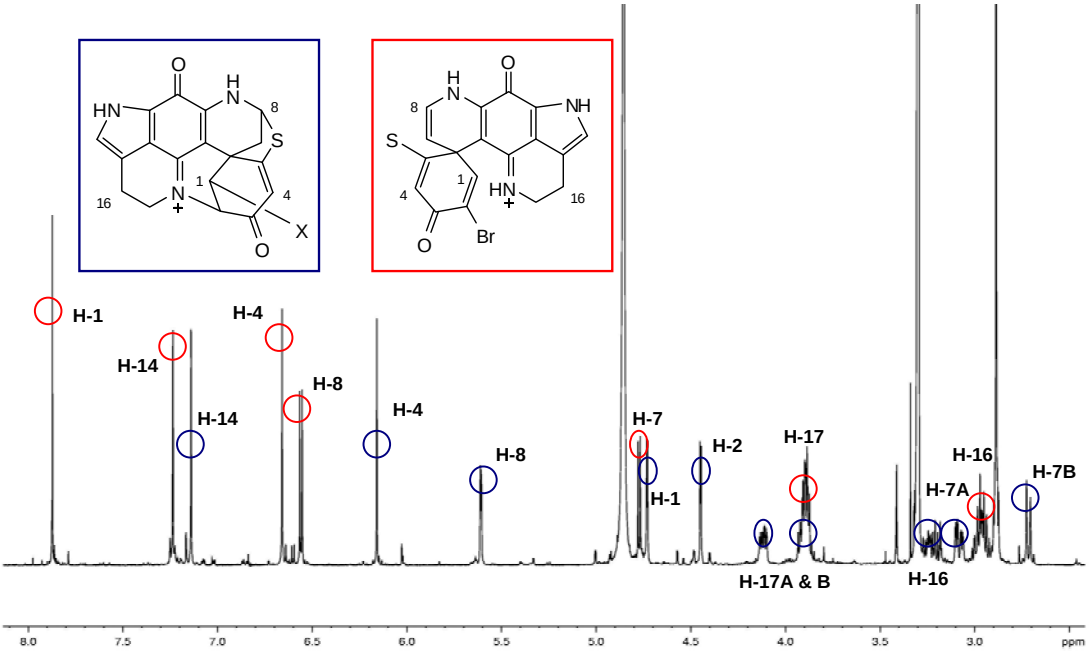


Fig. S2. ^{1}H–^{13}C HMBC spectrum of **17** TFA salt showing a crucial correlation from H-1 to C-26 to establish connectivity of the two subunits.

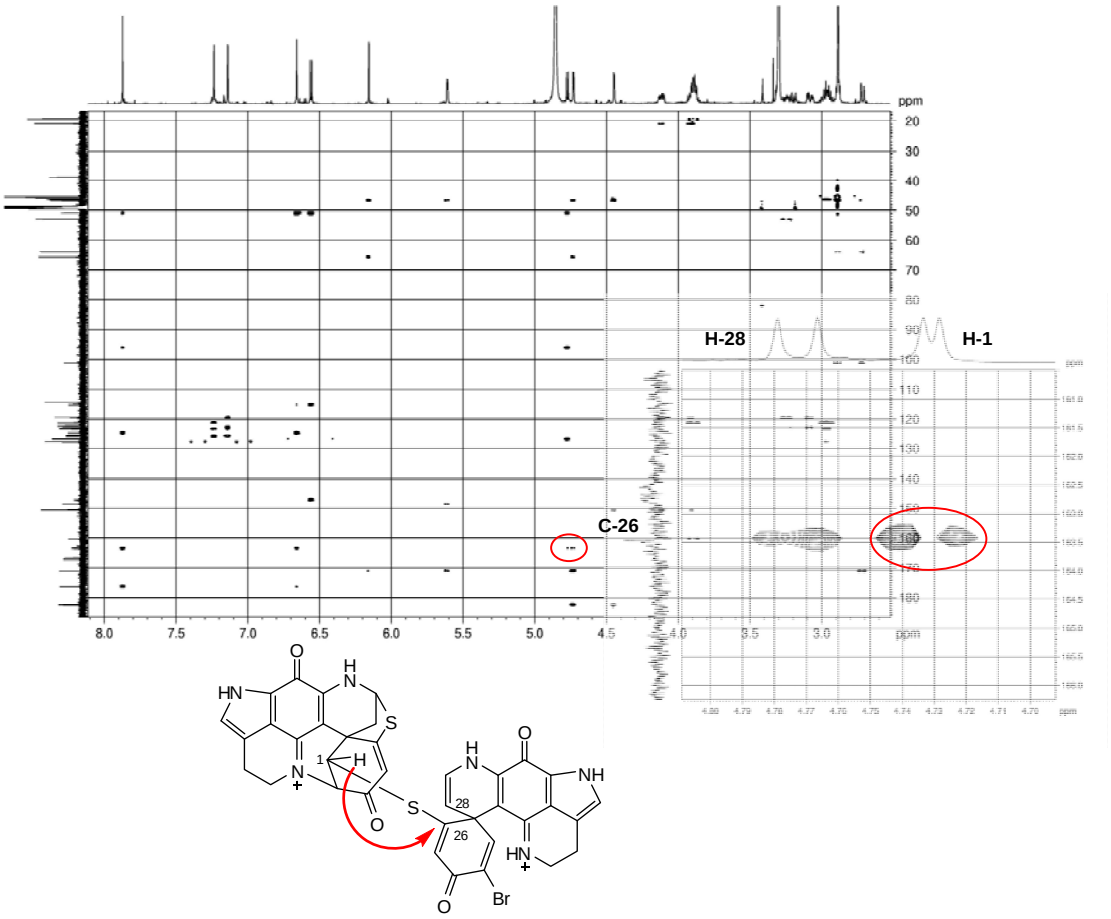


Table S1. NMR data for **17** TFA salt in CD_3OD.

no.	^{13}C δ	^{1}H δ [m, *J* (Hz)]	COSY	HMBC
1	46.1	4.73 (d, 3.0)	H-2	2, 3, 5, 6, 26
2	65.6	4.45 (d, 3.0)	H-1	1, 3, 6, 17, 19
3	182.4			
4	114.5	6.15 (s)		2, 5, 6
5	171.0			
6	46.6			
7A	38.9	2.89 (under impurity)	H-7B, H-8	5, 8, 20
7B		2.72 (d, 11.9)	H-7A, H-8	5, 8, 20
8	63.8	5.60 (dd, 3.6, 1.1)	H-7A, H-7B	5, 6, 10
10	148.6			
11	167.0			
12	125.6			
14	127.7	7.14 (s)		12, 15, 21
15	122.8			
16A	20.8	3.22 (m)	H-16B, H-17A, H-17B	15, 17, 21
16B		3.08 (ddd, 16.7, 6.7, 2.6)	H-16B, H-17A, H-17B	15, 17, 21
17A	52.9	4.12 (ddd, 13.9, 7.3, 2.6)	H-16A, H-16B, H-17B	16, 19, 21
17B		3.90 (m)	H-16A, H-16B, H-17A	16, 19, 21
19	150.5			
20	101.2			
21	119.5			
22	150.5	7.87 (s)		23, 24, 25, 26, 27, 41
23	124.7			
24	176.2			
25	122.3	6.66 (s)		23, 24, 27
26	163.5			
27	50.8			
28	115.1	4.77 (d, 7.5)	H-29	26, 27, 29, 41
29	126.8	6.56 (d, 7.5)	H-28	27, 28, 31
31	147.2			
32	166.5			
33	125.8			
35	127.6	7.24 (s)		32, 33, 35, 42
36	123.2			
37	19.3	2.97 (m)	H-38	35, 36, 38, 42
38	46.2	3.90 (m)	H-37	37, 40, 42
40	160.3			
41	95.8			
42	121.2			

^{1}H data at 600 MHz, ^{13}C at 150 MHz.

Fig. S3. ECD spectra of **17** (red) and (-)-discorhabdin H (**6**) (blue).

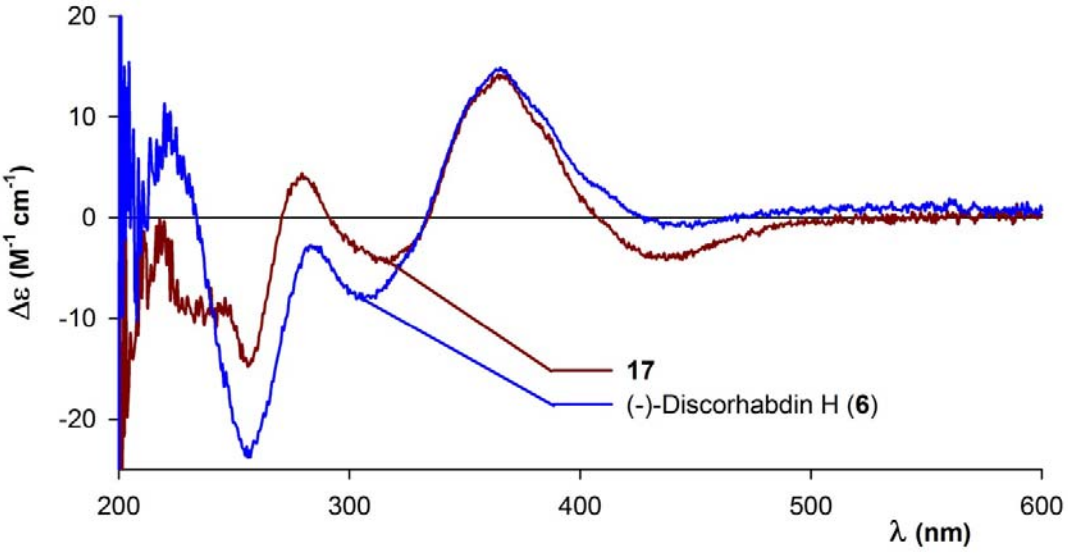


Fig. S4. ^{1}H NMR spectrum (CD_3OD, 400 MHz) of **11**.

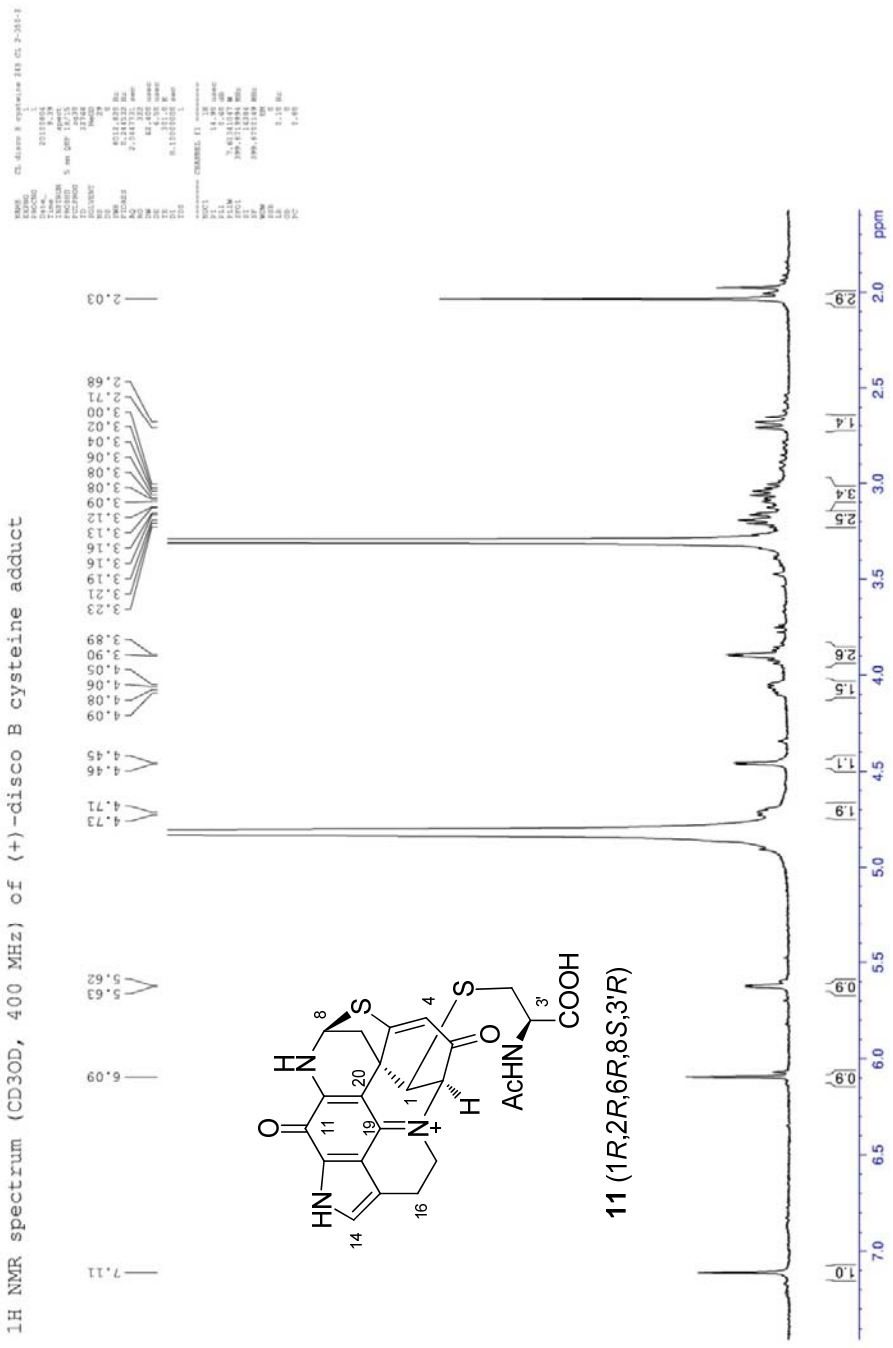


Fig. S5. ^{13}C NMR spectrum (CD_3OD, 100 MHz) of **11**.

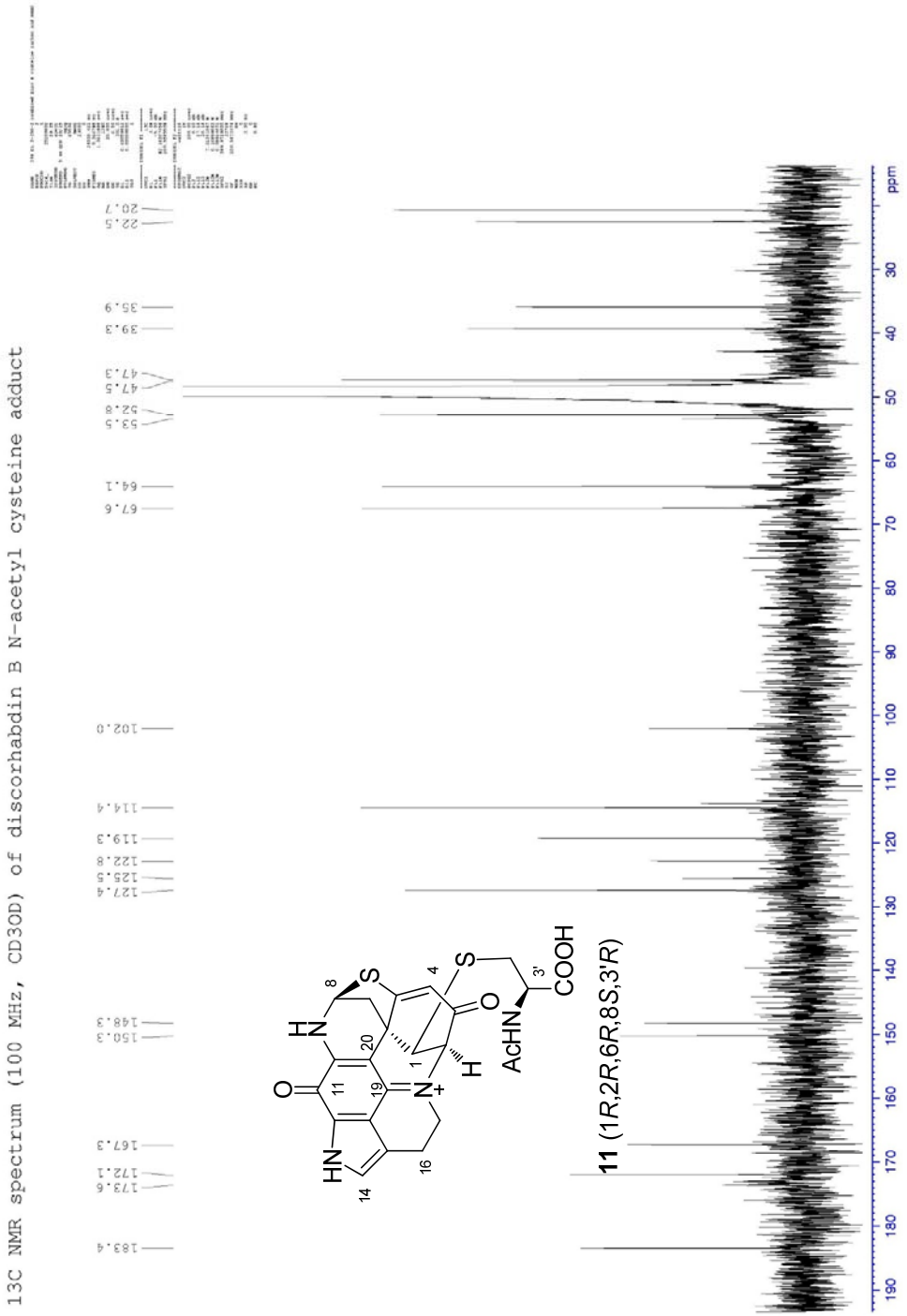


Fig. S6. COSY NMR spectrum (CD_3OD) of **11**.

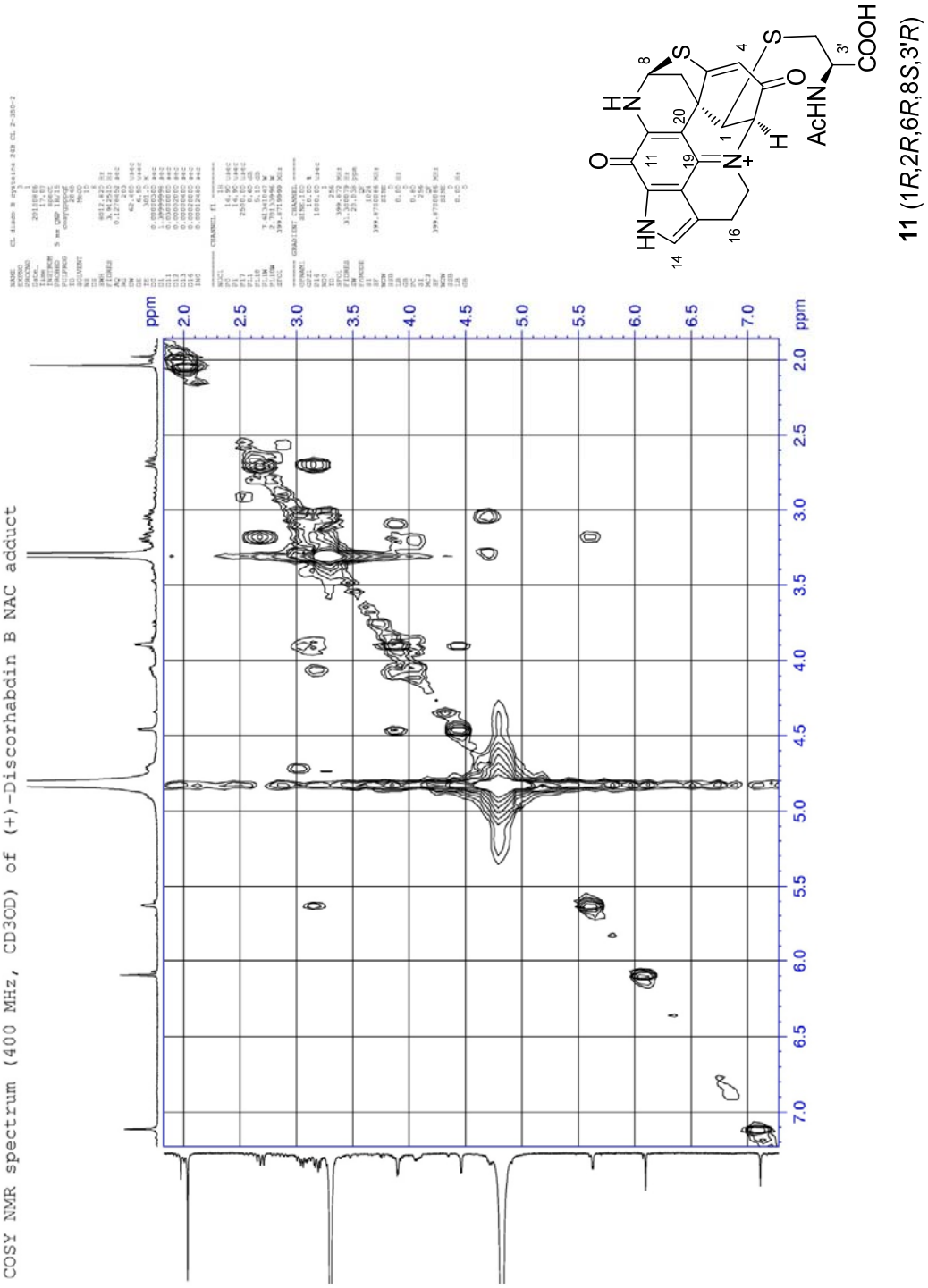
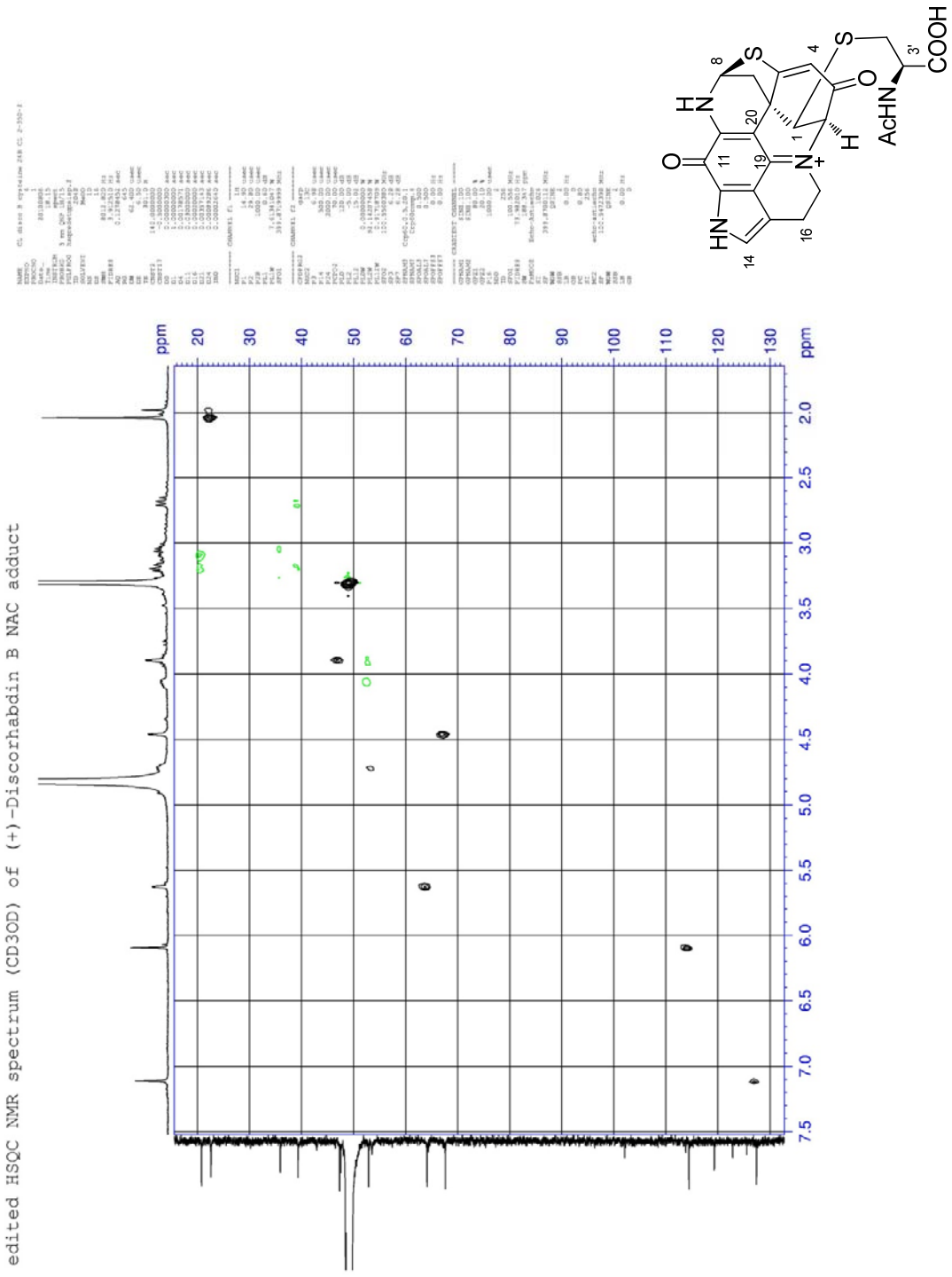
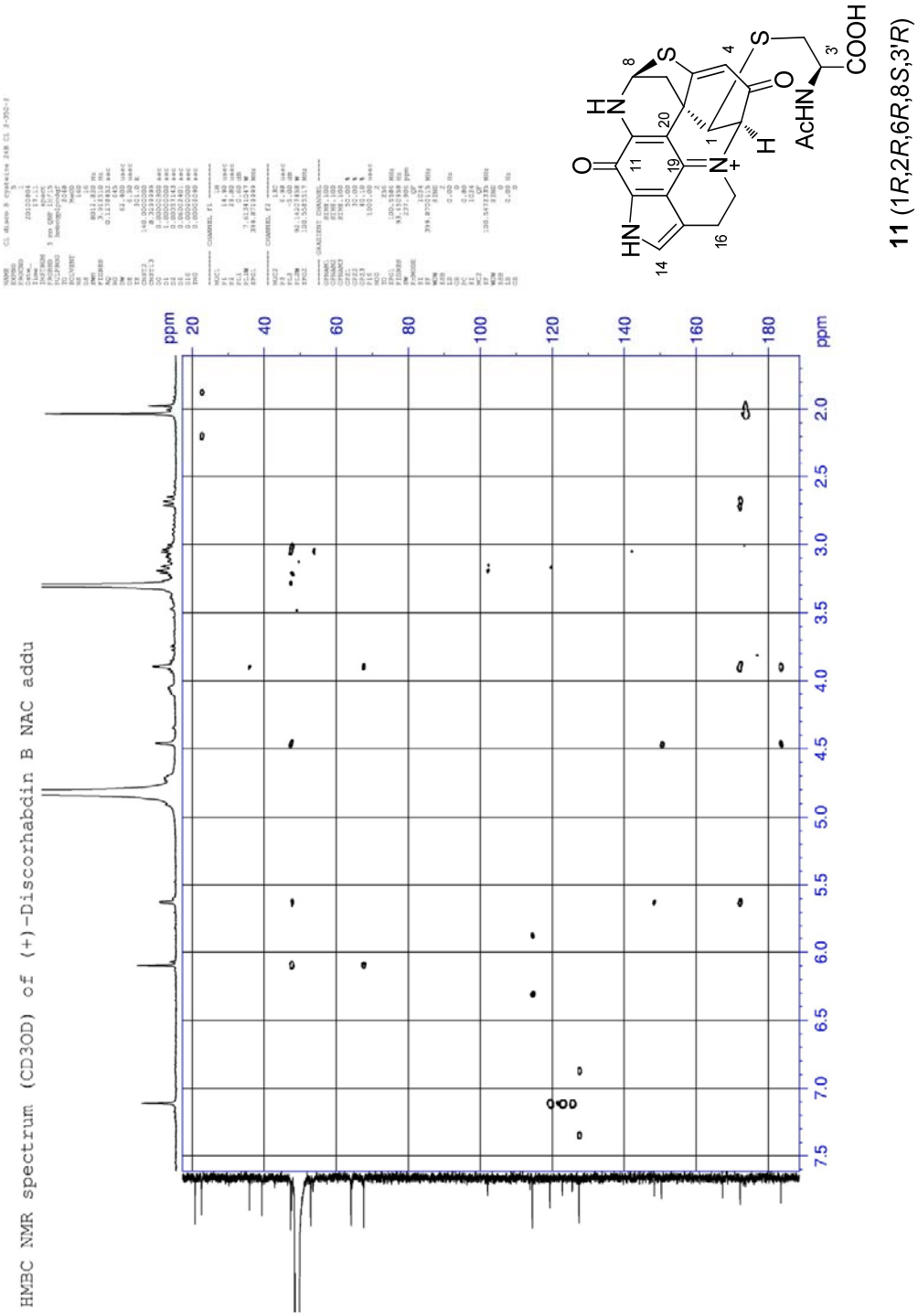


Fig. S7. Edited HSQC NMR spectrum (CD_3OD) of **11**.



11 (1*R*,2*R*,6*R*,8*S*,3'*R*)

Fig. S8. HMBC NMR spectrum (CD_3OD) of **11**.



11 (1*R*,2*R*,6*R*,8*S*,3'*R*)

Fig. S9. NOESY NMR spectrum (Tmix 600 ms, CD_3OD, 400 MHz) of **11**.

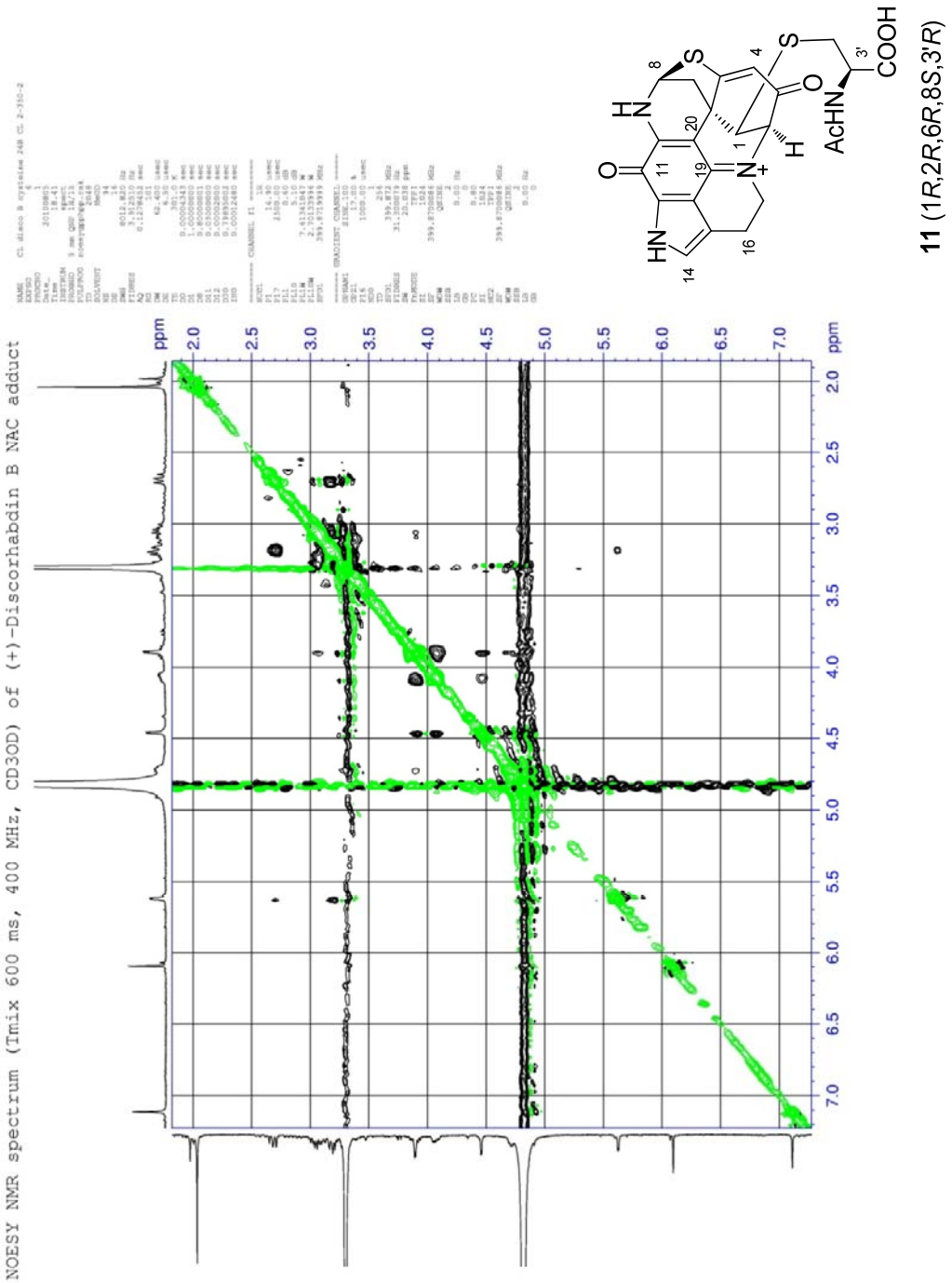


Fig. S10. ^{1}H NMR spectrum (CD_3OD, 400 MHz) of **12**.

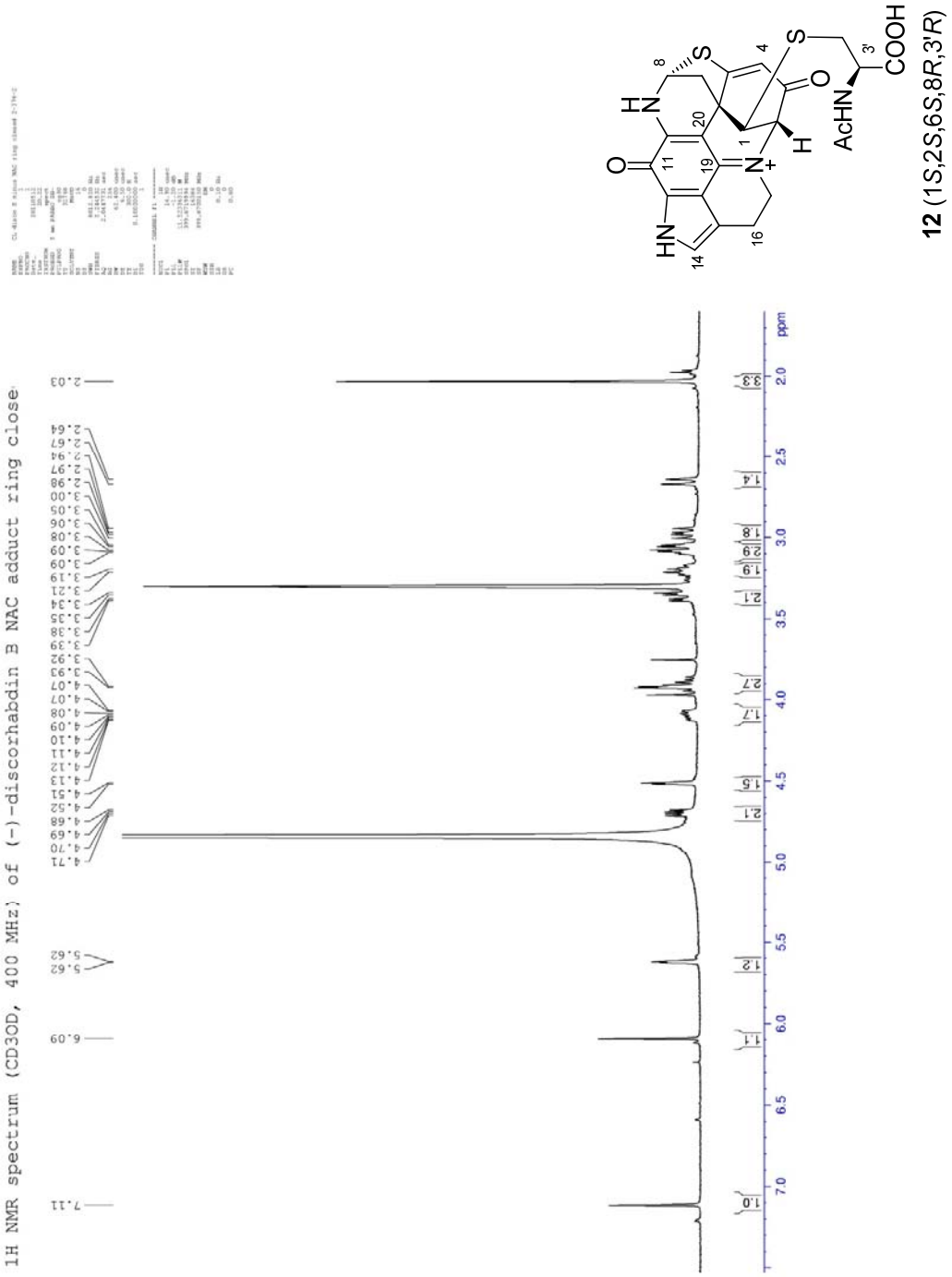


Fig. S11. ^{13}C NMR spectrum (CD_3OD, 100 MHz) of **12**.

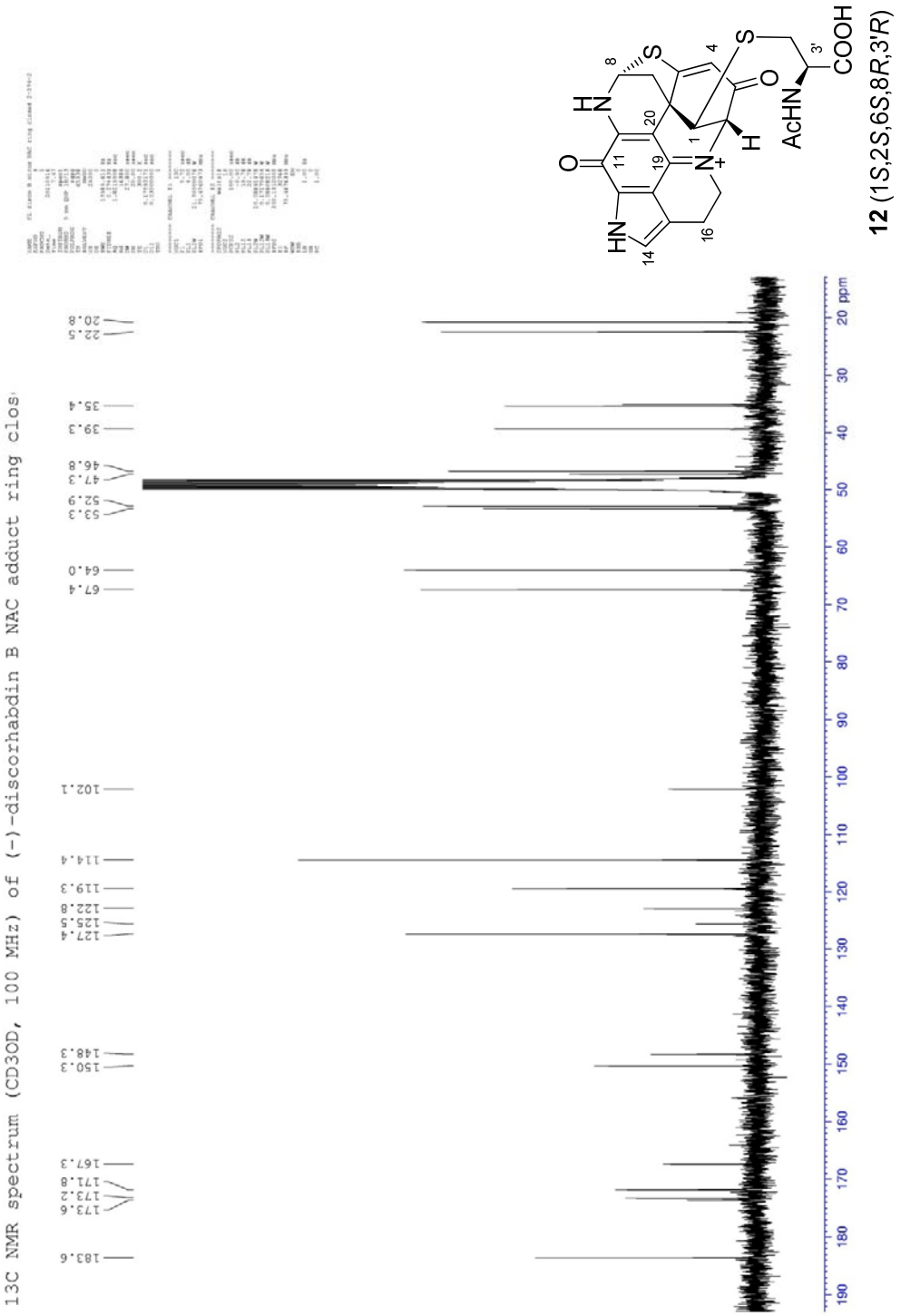


Fig. S12. COSY NMR spectrum (CD_3OD) of **12**.

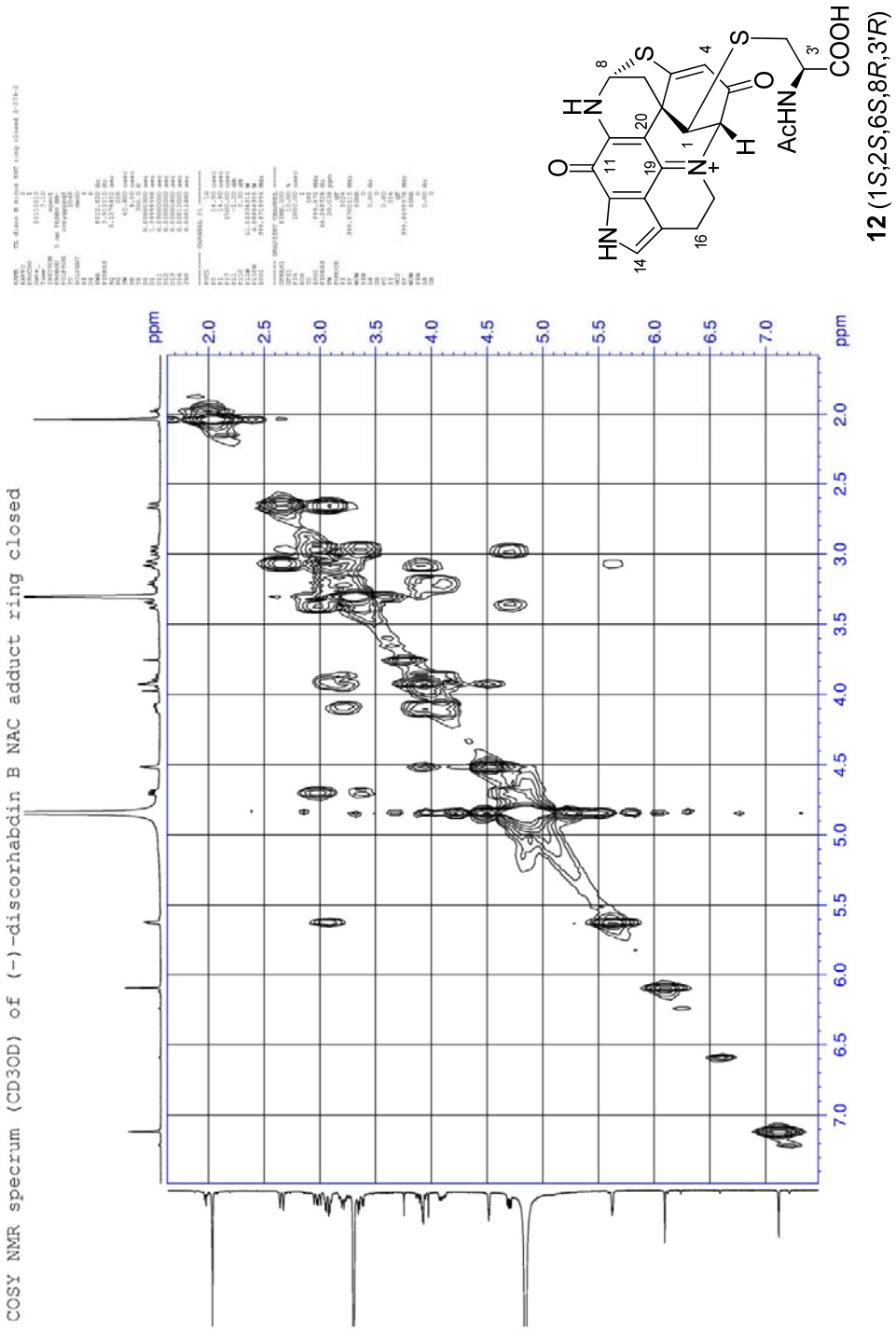
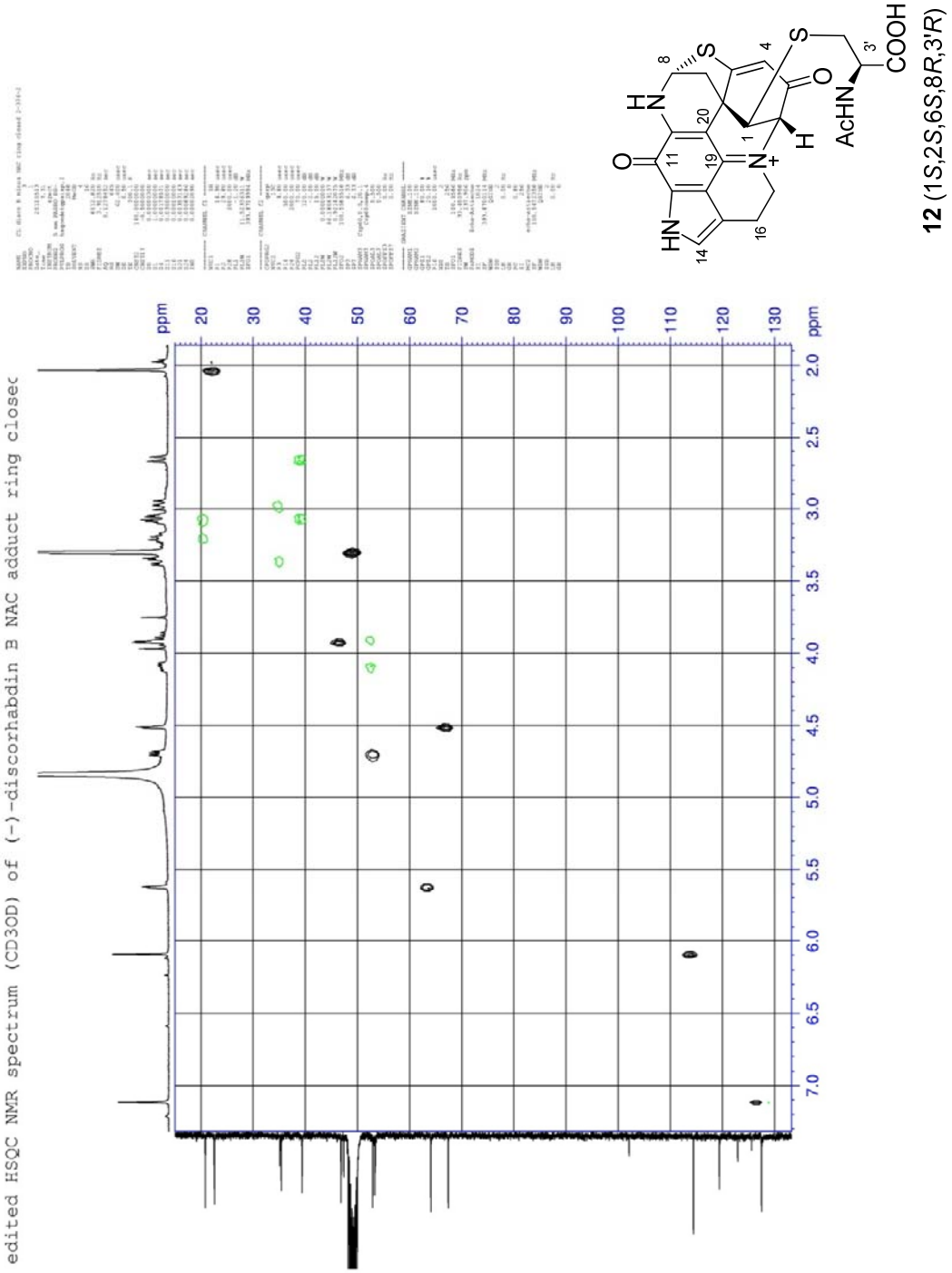


Fig. S13. Edited HSQC NMR spectrum (CD_3OD) of **12**.



12 (1*S*,2*S*,6*S*,8*R*,3'*R*)

Fig. S14. HMBC NMR spectrum (CD_3OD) of **12**.

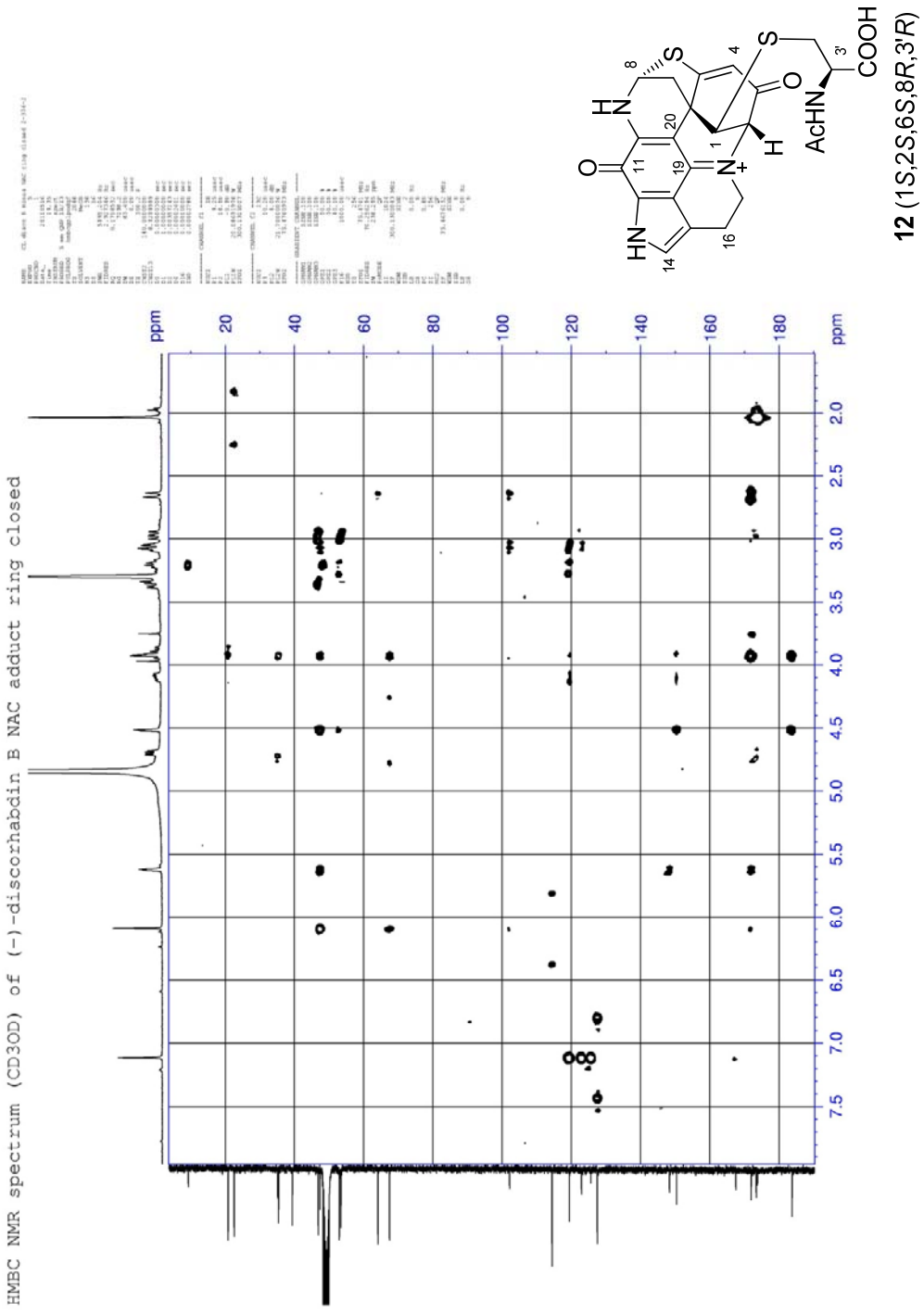


Fig. S15. ^{1}H NMR spectrum (CD_3OD, 400 MHz) of **13**.

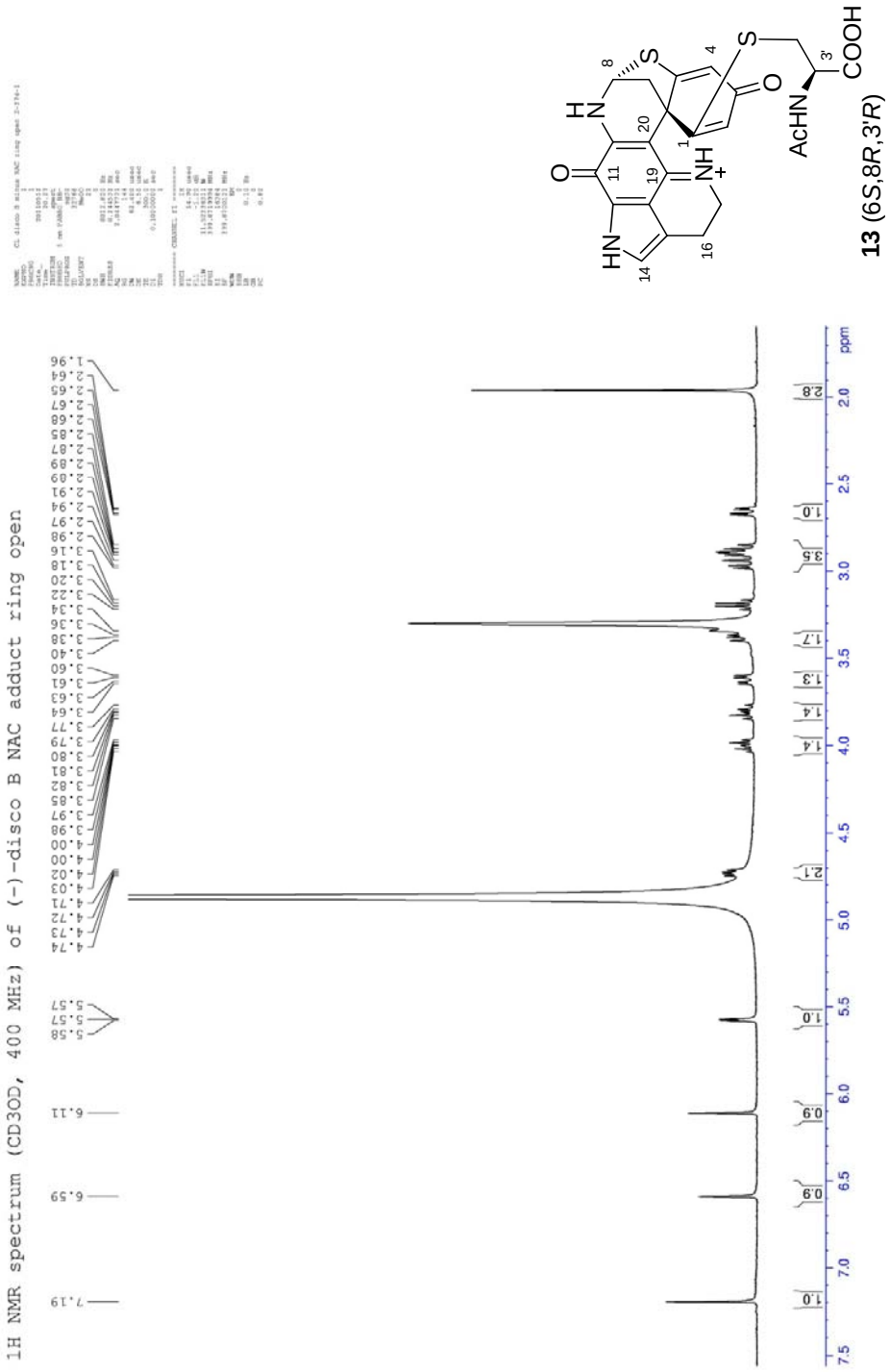


Fig. S16. ^{13}C NMR spectrum (CD_3OD, 100 MHz) of **13**.

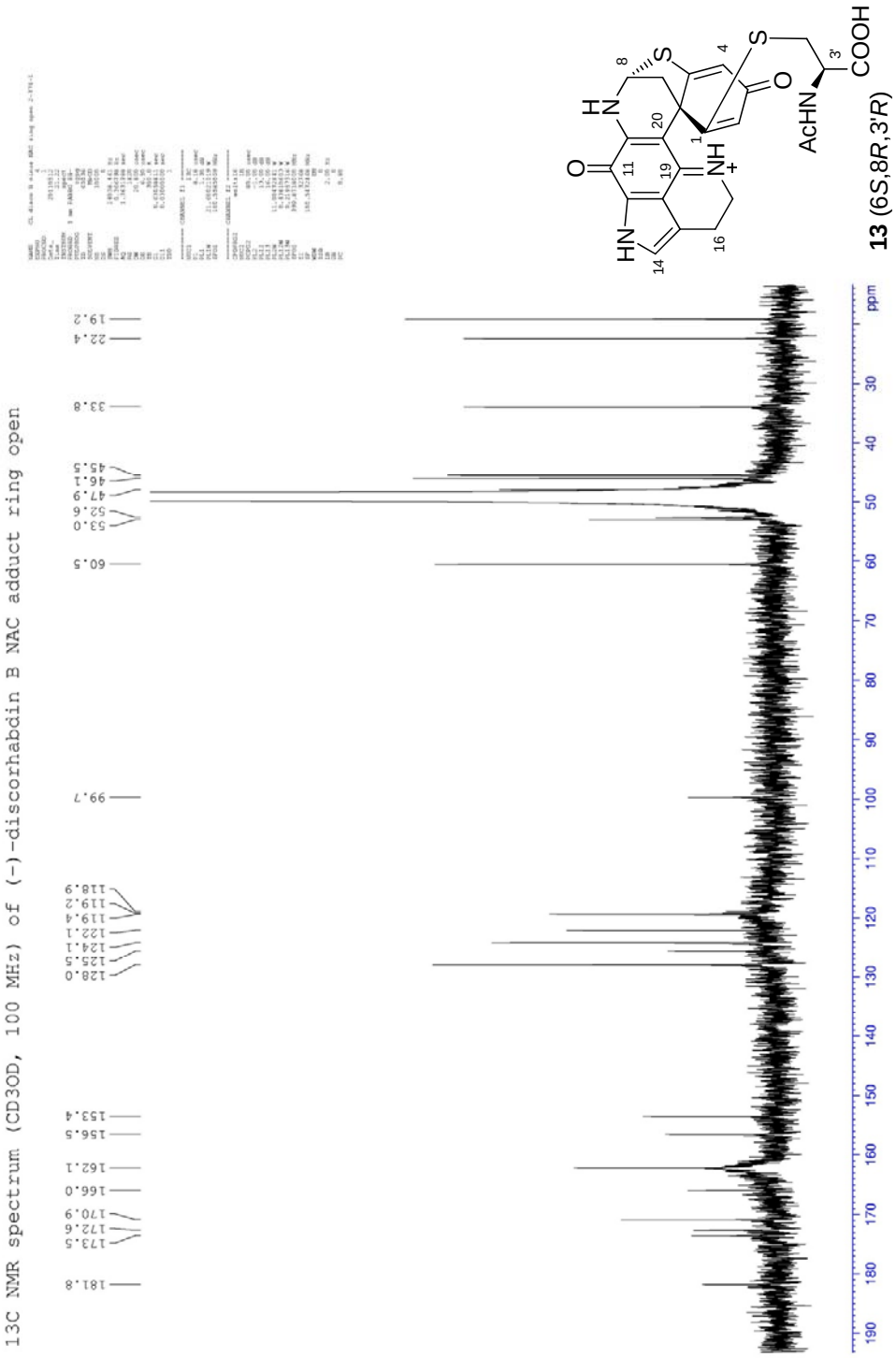


Fig. S17. COSY NMR spectrum (CD_3OD) of **13**.

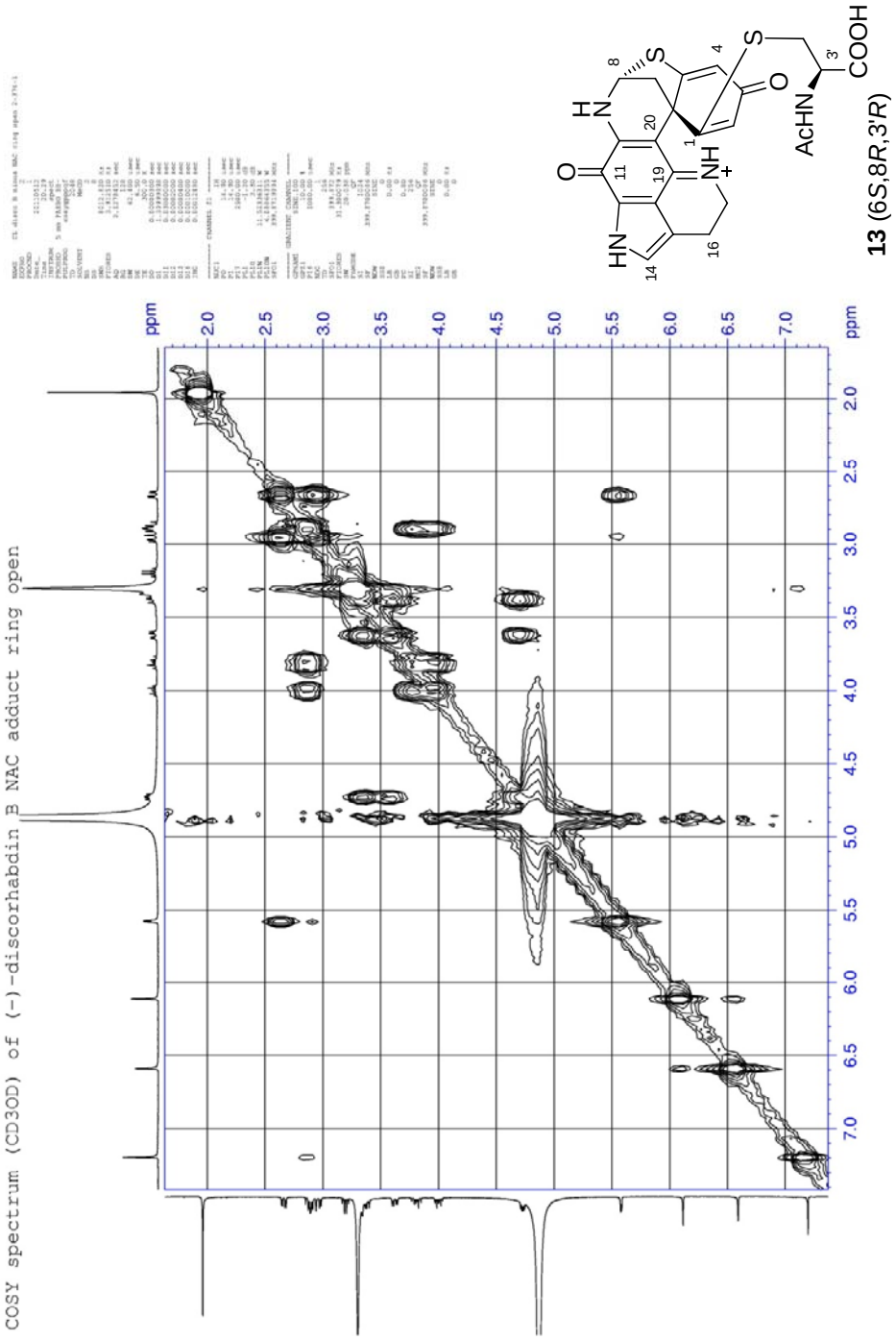


Fig. S18. Edited HSQC NMR spectrum (CD_3OD) of **13**.

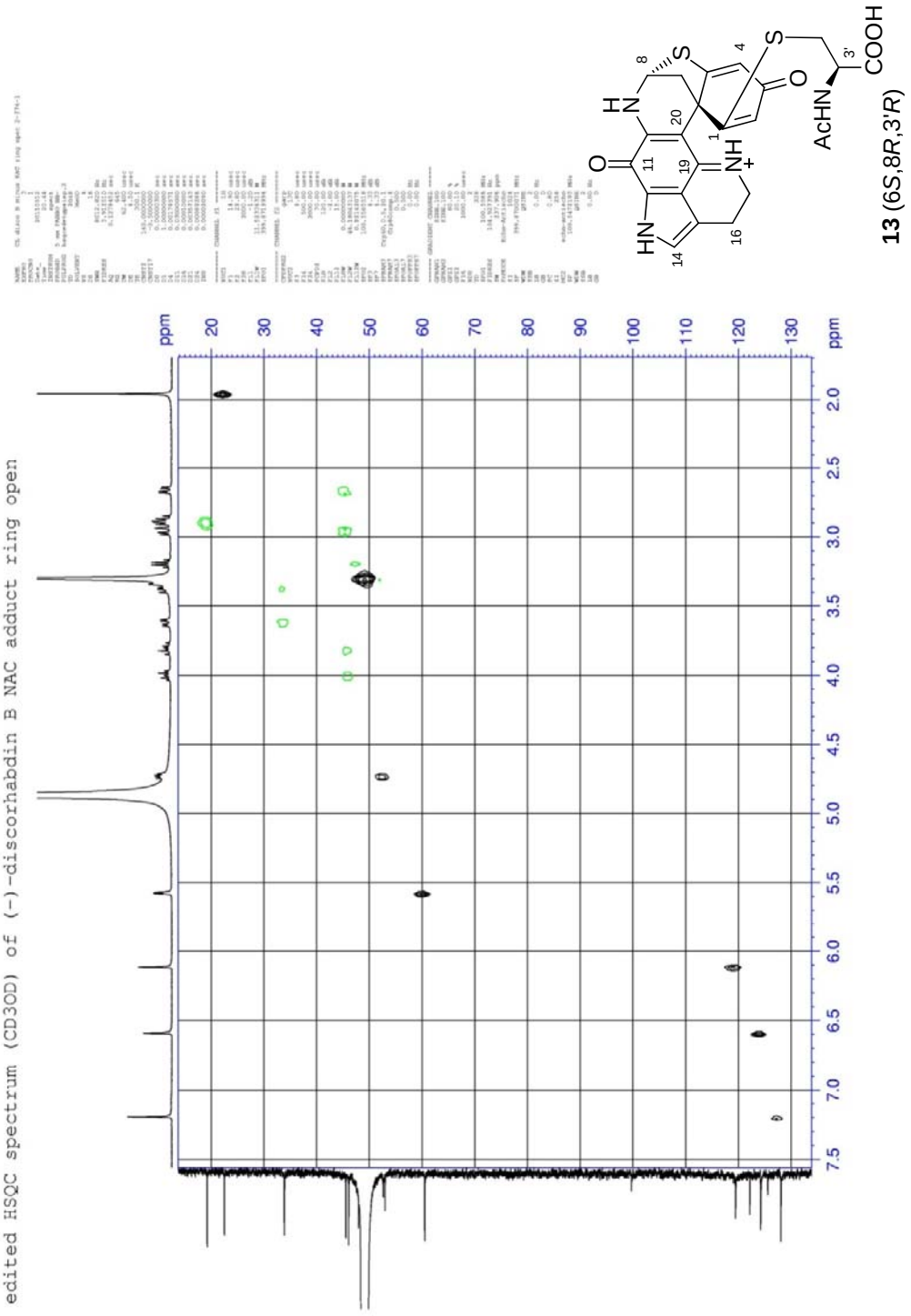


Fig. S19. HMBC NMR spectrum (CD_3OD) of **13**.

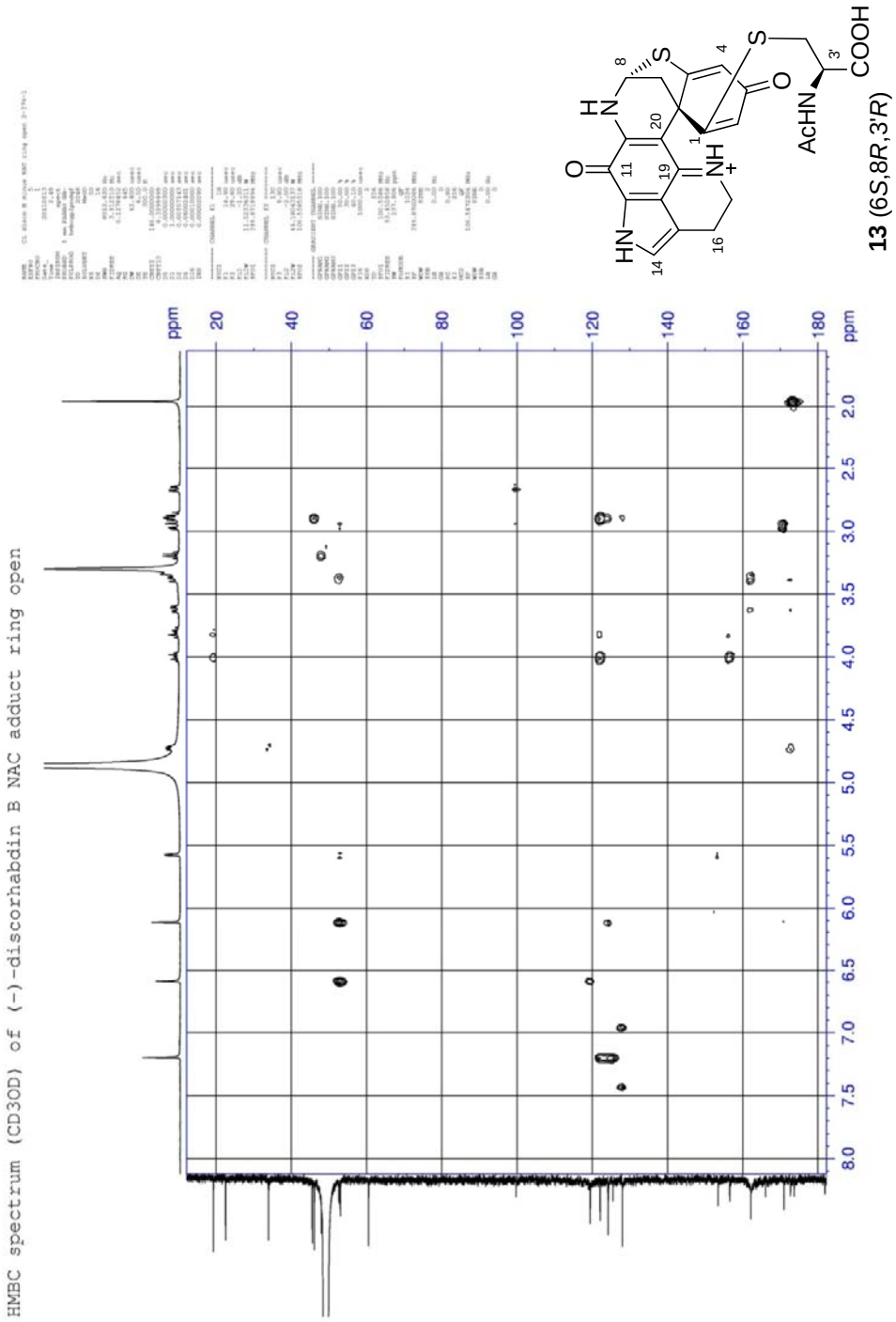


Fig. S20. ^{1}H NMR spectrum (CD_3OD, 600 MHz) of **17**.

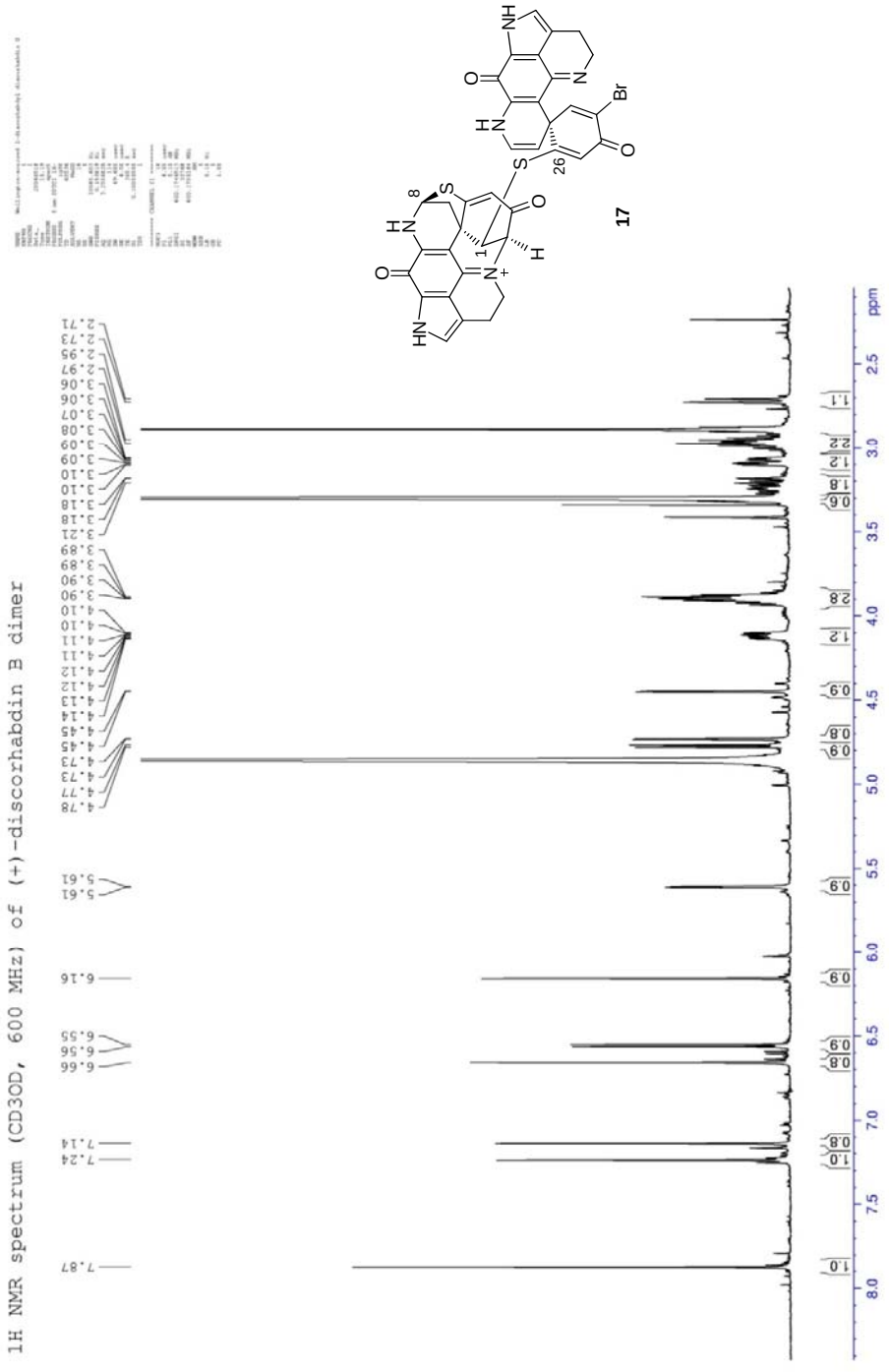


Fig. S21. ^{13}C NMR spectrum (CD_3OD, 150 MHz) of **17**.

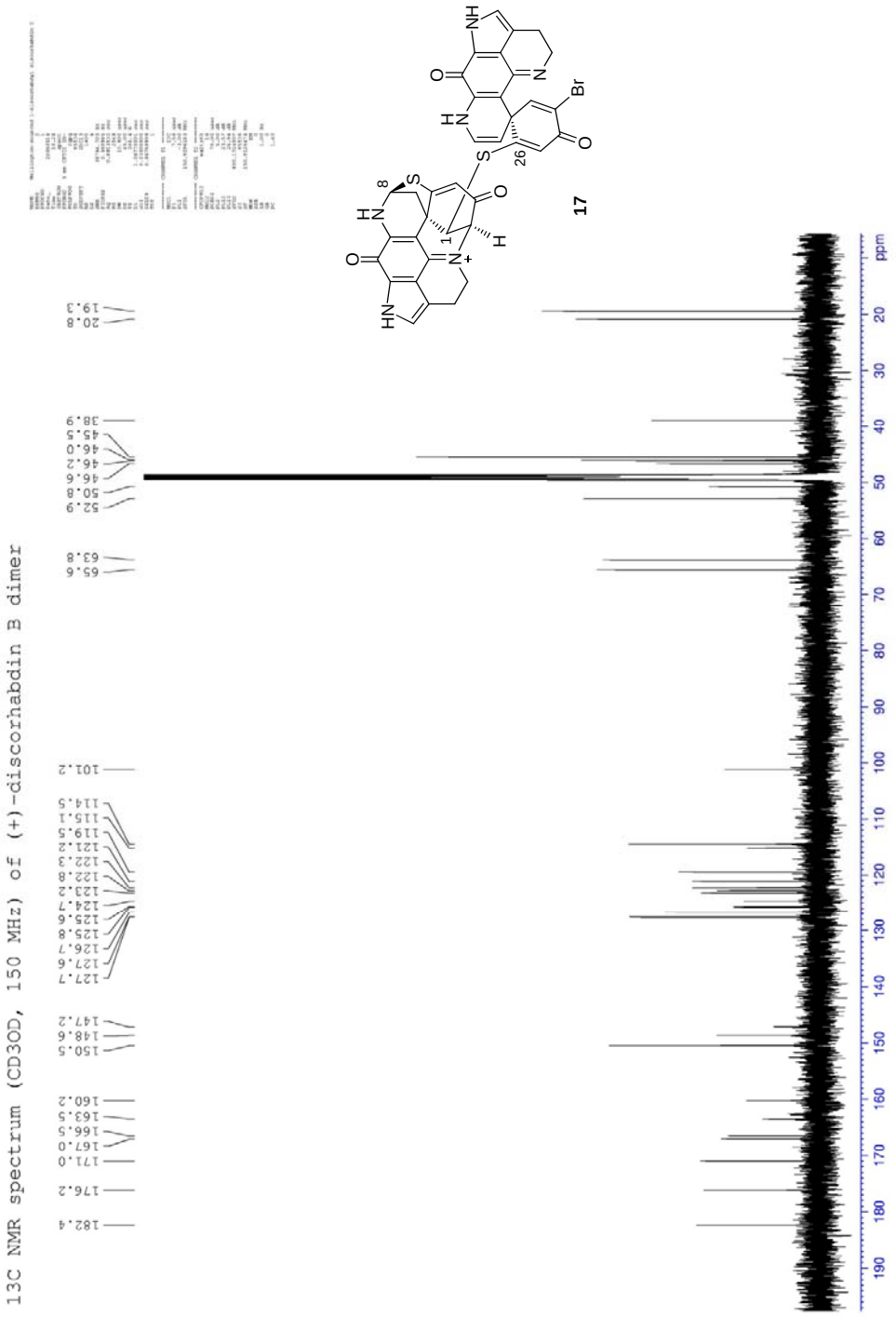


Fig. S22. LR-COSY NMR spectrum (opt for 2 Hz, CD_3OD) of **17**.

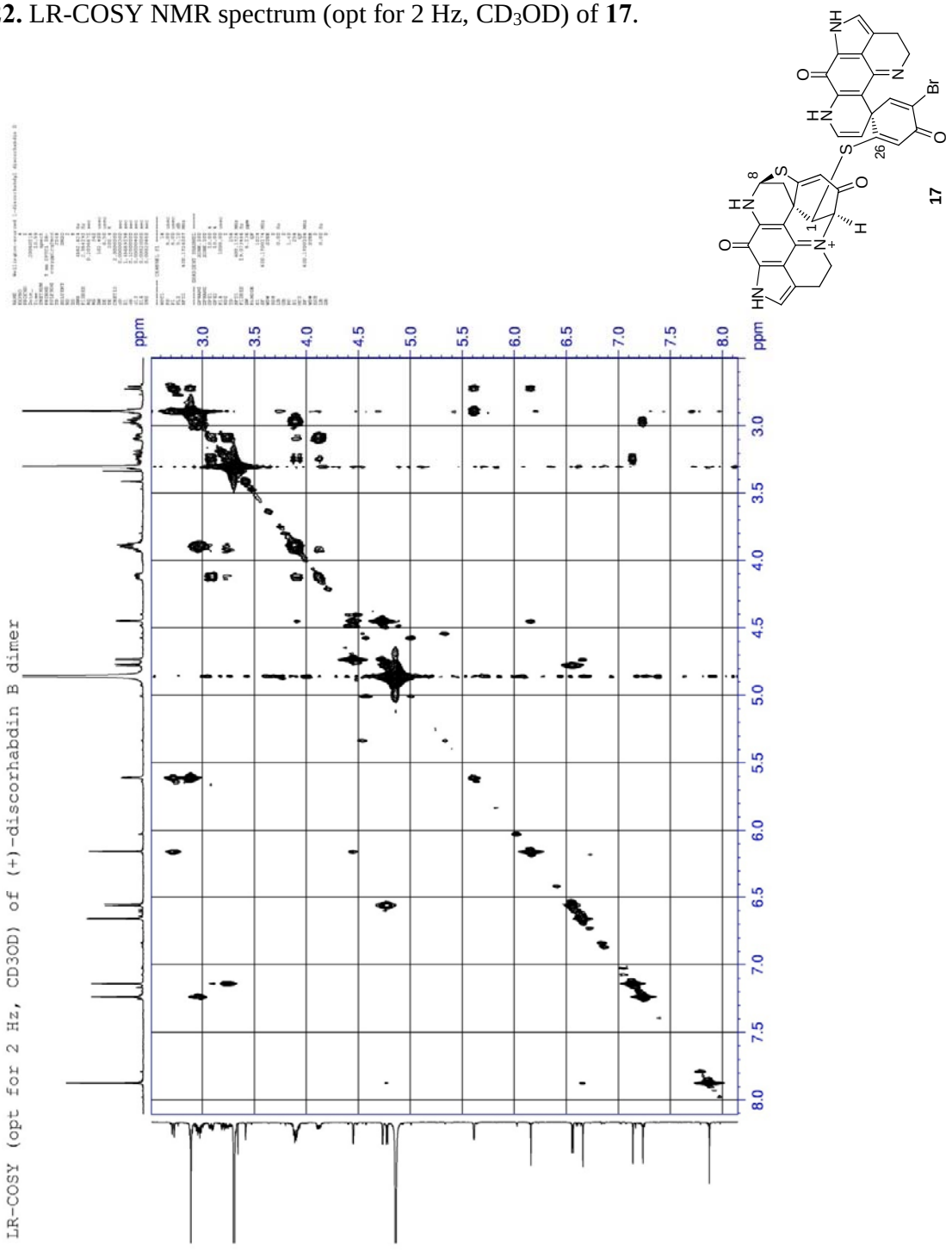


Fig. S23. Edited HSQC NMR spectrum (CD_3OD) of **17**.

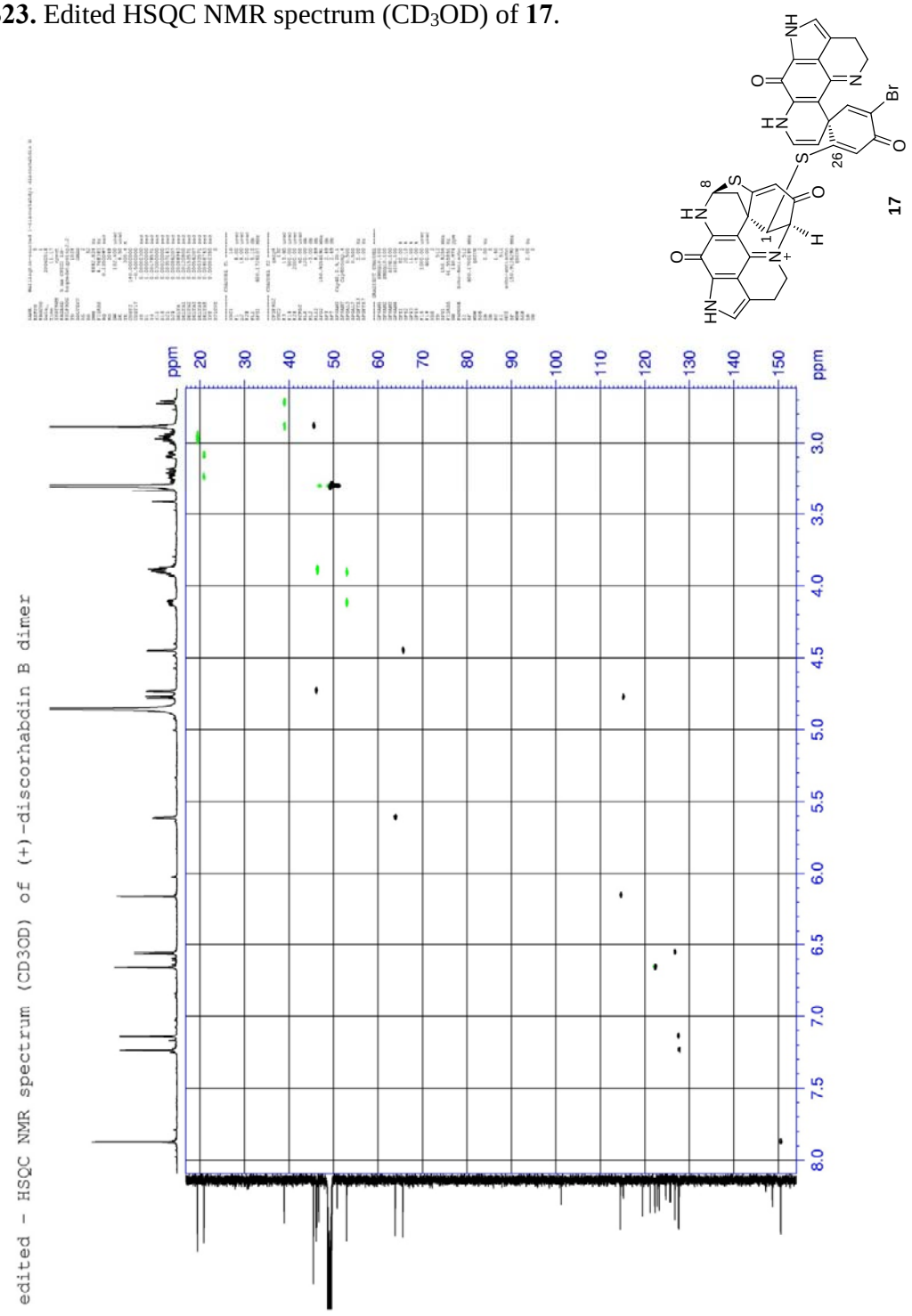


Fig. S24. HMBC NMR spectrum (CD_3OD) of **17**.